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(54) Title: RADIATION CURABLE RESIN COMPOSITION (57) Abstract <p>A radiation curable resin composition suitably used for a protective coating which has a high hardness and excels in the adhesion to a substrate, adhesion to printing ink, scratch resistance, light resistance, thermal resistance, and resistance to the fingerprint adhesion and which is suitable for use as information recording carriers such as thermosensitive recording type cards, thermosensitive photographic paper, or the like. The radiation curable resin composition comprises (A) a meth(acrylate) of a bisphenol A diglycidyl ether polymer, (B) a multiacrylate compound (e.g., dipentaerythritol monohydroxypentacrylate), (C) optionally, a radiation active initiator, and (D) inorganic particles, wherein the proportions of components (A), (B), (C), and (D) are from 10 to 50 parts by weight, from 50 to 90 parts by weight, from 0.1 to 10 parts by weight, and from 0.1 to 10 parts by weight, respectively, when the sum of the amounts of components (A) and (B) is 100 parts by weight.</p>		

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RADIATION CURABLE RESIN COMPOSITION5 **Field of the Invention**

 The present invention relates to a radiation curable resin composition which has a high hardness and excellent adhesion to a substrate, and produces cured products exhibiting high adhesion to a printing ink, and superior resistance to damages from
10 scratching (hereinafter called "scratch resistance") from nails or the like, light resistance, thermal resistance, and resistance to fingerprint adhesion, and, especially, to a radiation curable resin
15 composition which is suitable for use as a printable and heat-resistant protective coating used for information recording carriers, for example, heat sensitive recording type cards, heat sensitive photographic paper, or the like.

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Background of the Invention

 Information recording carriers, such as rewritable type thermosensitive recording cards, thermosensitive photographic paper, or the like, are
25 provided with a protective coating layer to improve the heat resistance and resistance to mar resistance to the surface of a recording medium, and the like. As materials used for such a protective coating layer, UV-
30 ray curable acrylate type resin compositions, which are conventionally utilized for protecting the surface of plastic substrates or as a protective coating for optical disks, are used. Japanese Patent Application

Laid-open No. 149280/1992 discloses an overcoating composition used for optical disks, comprising tripropylene glycol diacrylate and 2-(2-ethoxyethoxy)ethyl acrylate and a photo initiator. The overcoating composition disclosed here possesses the necessary features in that it has a low skin stimulus and a low viscosity and, also, it has sufficient film hardness and excels in resistance to frictional damage when it is used as an overcoating for optical disks. Such an overcoating material has excellent mar resistance at normal temperature, but cannot withstand an impact by a thermal head in the case where it is used as a protective coating for a thermosensitive recording card, exhibiting a problem to be solved in the mar resistance at a high temperature. Furthermore, the surface of the protective coating prepared from this overcoating composition is inferior in resistance to fingerprint adhesion. When touching the surface of the protective coating with a finger, the trace of the fingerprint adheres with ease. This not only damages the transparency of the surface but also impedes the discrimination of character information recorded on a layer under the protective coat, which is a problem to be solved.

Also, Japanese Patent Application Laid-open No. 106161/1992 discloses a heat-curable multilayer coat produced by combining a specific primer material having an unsaturated double bond with an organopolysiloxane type hard coating. Products coated with this heat-curable multilayer coat have excellent mar resistance, wear resistance, surface glossiness, and resistance to weathering adhesion. The organopolysiloxane type hard coating disclosed here forms a strong coating associated with a siloxane bond as it is cured and the coating is expected to possess

excellent resistance to damage. This patent application also discloses that a microparticle inorganic oxide is added internally to a surface coating to improve the hardness of the surface of the coating. However, 5 because the curing is performed by heat, this causes not only the curing time to be prolonged so that productivity decreases, but also deterioration of a thermosensitive layer. Therefore, this method is not practical. Also, though the overcoating layer produced 10 with a polysiloxane structure has excellent resistance to frictional damage and good thermal resistance, the coating lacks flexibility and hence there is a problem that cracks occur easily when it is used for rewritable thermosensitive recording cards or thermosensitive 15 photographic paper. Furthermore, the surface of the overcoating obtained in this manner tends to repel printing ink and hence satisfactory printing on this surface is difficult.

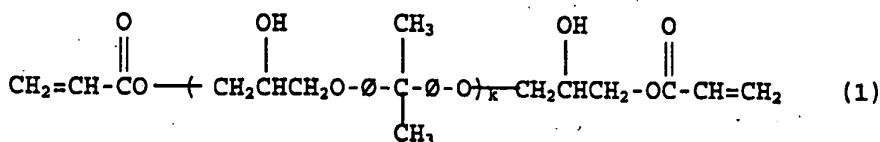
Also, Japanese Patent Publication No. 20 103328/1995 discloses an activated energy ray-curable coating composition comprising 20-80 parts of an acrylate of a bisphenol A diglycidyl ether compound, 5-50 parts of a dipentaerythritol compound having six acrylate functional groups and other optional 25 components as well. This patent publication discusses that the composition can be applied with ease because of its low viscosity, can be cured in an extremely short period of time by irradiation with UV rays, electron beams, or the like, excels in adhesion to a 30 substrate and in processability such as bending characteristics, and the like, and has excellent glossiness. However, there are problems inasmuch as the compositions of this publication have inferior scratch resistance and resistance to fingerprint adhesion.

Summary of the Invention

It is an object of the present invention to provide a radiation curable resin composition used suitably for a protective coating which has a high hardness and excellent adhesion to a substrate, and produces cured products exhibiting high adhesion to a printing ink, and superior scratch resistance, light resistance, heat resistance, flexibility, and resistance to fingerprint adhesion, the protective coating being used for a wide variety of substrates. In particular, those substrates wherein such features are valuable which may include various types of storage media such as optical disks (e.g. compact disks, commonly referred to as CD's), and cards and rewritable storage medium including optical disks and cards, and other types of storage media such as thermosensitive type information recording carriers, for example, thermosensitive recording type cards, thermosensitive photographic paper, or the like.

Accordingly, the above objects and advantages, as well as others that will be appreciated from the present invention can be attained by the a radiation curable resin composition comprising:

- (A) a (meth)acrylate of a bisphenol diglycidyl ether polymer, preferred (meth)acrylates of bisphenol diglycidyl ether polymers include those represented by the following formula (1):



- wherein \emptyset represents a paraphenylene group and k denotes a value from 1 to 10 (herein the term (meth)acrylates of bisphenol diglycidyl ether polymers is understood to include a monomer, for instance, wherein k is equal to one; and mixtures wherein the value of k represents an average k value, not necessarily an integer value, for the components present in the mixture);
- (B) a multi-acrylate compound having from 4 to 8 acrylate groups, preferably 4 to 5 acrylate groups and at least one hydroxy group;
- (C) optionally, a radiation polymerization initiator; and
- (D) inorganic particles;
- wherein the proportions of components (A), (B), (C), and (D) are from 10 to 50 parts by weight, from 50 to 90 parts by weight, from 0.1 to 10 parts by weight, and from 0.1 to 10 parts by weight, respectively, and the sum of the amounts of components (A) and (B) is 100 parts by weight.

The acrylate of a bisphenol diglycidyl ether polymer, which is the component (A) used in the present invention preferably includes acrylates of bisphenol -A, -F, and -S diglycidyl ether polymer and more preferably those represented by the above formula (1), and in particular wherein k is less than 5. Preferably, the molecular weight of component (A) is between 400 and 3,000. Acrylates of a bisphenol A diglycidyl ether polymer are commercially available under the trademarks of SP-1507, SP-1509, SP-1519-1, SP-1563, SP-2500, VR-60, VR-77, VR-90 (manufactured by Showa High polymer Co., Ltd.), Viscoat 540 (manufactured by Osaka Organic Chemical Industry Co., Ltd.), and Epoxy Ester 3000A, 3000 M (manufactured by

Kyoeisha Chemical Co., Ltd.).

These compounds may be used either independently or in combinations of two or more.

The proportion of component (A), when the sum of the amounts of components (A) and (B) is 100 parts by weight, is preferably from 10 to 40 parts by weight and more preferably from 10 to 30 parts by weight, although it is generally from 10 to 50 parts by weight as aforementioned. If the proportion of component (A) exceeds 50 parts by weight, the surface hardness after curing decreases and hence the surface tends to be damaged. On the other hand, if the proportion is less than 10 parts by weight, the flexibility of the coating after curing decreases so that the coating tends to break. Therefore, a proportion out of the above defined range is undesirable.

Component (B) is a multi-acrylate compound which is used herein to refer to compounds that include from 4 to 8 acrylate functional groups. Preferred multi-acrylate compounds include those having from 4 to 6 acrylate functional groups and at least one hydroxy group. A particularly preferred multi-acrylate compound is dipentaerythritol monohydroxypentaacrylate. Examples of commercially available dipentaerythritol monohydroxypentaacrylate include under the trademarks of SR399, SR399E, SR9041, (manufactured by Sartomer Co.). These compounds may be used either independently or in combinations of two or more.

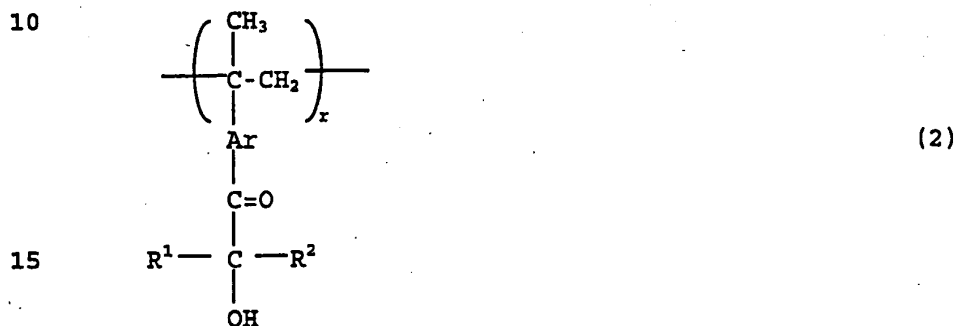
The proportion of component (B), when the sum of the amounts of components (A) and (B) is 100 parts by weight, is preferably from 60 to 90 parts by weight and more preferably from 70 to 90 parts by weight, although it is generally from 50 to 90 parts by weight as aforementioned. If the proportion of

component (B) exceeds 90 parts by weight, the coating after curing tends to break, whereas if the proportion is less than 50 parts by weight, the hardness of the coating after curing decreases and hence the surface tends to be damaged. Therefore, a proportion out of the above defined range is undesirable.

As the radiation active initiator, any compounds which decompose by exposure to radiation and produce radicals to start polymerization may be used. Further, a photosensitizer may be used as required. Here, "radiation" includes UV rays, visible rays, X-rays, electron beams, α -rays, β -rays, γ -rays, and the like. Given as examples of compounds used as such a radiation active initiator are 1-

hydroxycyclohexylphenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 1,1-dimethoxydeoxybenzoin, 3,3'-dimethyl-4-methoxybenzophenone, 1-(4-dodecylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholino-propan-1-one, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, ethyl-2,4,6-trimethylbenzoylphenyl phosphinate, bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, bisacylphosphine oxide, methylbenzoyl formate, 4-benzoyl-4'-methyldiphenyl sulfide, benzyl methyl ketal, fluorenone, fluorene, benzaldehyde, benzoin ethyl ether, benzoin propyl ether, Michler's ketone, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, acetophenone, 3-methylacetophenone, benzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, 3,3',4,4'-tetra (t-butyl peroxy carbonyl) benzophenone (BTTB), acetophenone benzyl ketal, triphenylamine, carbazole, 4-chlorobenzophenone, anthraquinone,

xanthone, diethylthioxanthone, 2-isopropylthioxanthone, 4-isopropylthioxanthone, 2-chlorothioxanthone, 1-chloro-4-propoxythioxanthone, and combinations of BTTB and color substance photosensitizers such as xanthene, 5 thioxanthene, cumarin, ketocumarin, or the like. Also, compounds represented by the following formula (2) may be used.



wherein R^1 and R^2 independently represent an alkyl group having 1-5 carbon atoms, Ar represents a divalent aromatic group such as a phenylene group, a biphenylene group, a naphthylene group, or the like, and r denotes an integer from 2 to 50, preferably from 2 to 20.

Examples of the alkyl group in Formula (2) include a methyl group, ethyl group, n-propyl group, i-propyl group, t-butyl group, n-pentyl group, i-pentyl group, and the like. Among these groups, an alkyl group having 1-3 carbon atoms is preferable.

Among the aforementioned compounds used for the radiation active initiator, benzyl methyl ketal, 30 benzophenone, 1-hydroxycyclohexyl phenyl ketone, 2,4,6-trimethylbenzoyl diphenylphosphine oxides, ethyl-2,4,6-trimethylbenzoylphenyl phosphinate, bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxides, 2-methyl-1-[4-(methylthio) phenyl]-2-

morpholinopropan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, and the like are especially desirable. Also, examples of commercially available products include Irgacure 184, 651, 500, 907, 369, 784, 2959 (manufactured by Ciba-Geigy), Lucirin TPO, LR 8893 (manufactured by BASF), Darocur 1116, 1173 (manufactured by Merck Co.), Ubecryl P36 (manufactured by UCB Co.), ESCACURE KIP150, ESCACURE KIP100F (manufactured by LAMBERTI Co.), and the like.

10 These radiation active initiator may be
used either independently or in combinations of two or
more.

The proportion of component (C), when the sum of the amounts of components (A) and (B) is 100 parts by weight, is preferably from 0.5 to 8 parts by weight, and more preferably from 1 to 6 parts by weight, although it is generally from 0.1 to 10 parts by weight. If the proportion exceeds 10 parts by weight, there may be adverse effects on the curing properties of the liquid resin and the properties and handling characteristics of the cured product. On the other hand, if the proportion is less than 0.1 parts by weight, the curing rate is excessively low, leading to remarkably reduced productivity.

25 The average particle diameter of the
inorganic particles, which are component (D) used in
the present invention, is preferably from 0.1 to 10 μm ,
and more preferably from 0.2 to 5 μm . If the average
particle diameter is smaller than 0.1 μm , the mar
30 resistance and surface sliding properties are
insufficient, whereas if the average particle diameter
is greater than 10 μm , there is the case where the
transparency of the coating remarkably decreases.

Examples of inorganic particles include

- 10 -

silica particles, glass particles, alumina, magnesium carbonate, calcium carbonate, calcium phosphate, aluminum hydroxide, talc, titanium oxide, and the like are given. Among these, silica particles, glass particles, calcium carbonate, and talc are desirable. The silica particles are commercially available under the trademarks of Nipsil E220A, E220, K300, E1011, HD, E743, SS-10F, SS-178B (manufactured by Nippon Silica Industrial Co., Ltd.), Sildex H31, H32, L-31 (manufactured by Asahi Glass Co., Ltd.), SO-E2, SO-E3, SO-E5 (manufactured by Admatechs Co., Ltd.), and the like.

Talc is commercially available under the trademarks of LMS-300, LMS-200, LMS-100, LMP-100, LMG-100, LMR-100, PKP-53 (manufactured by Fuji Talc Industrial Co., Ltd.).

Calcium carbonate is commercially available under the trademarks of Calcies, Calcies-P, PL,-X, Star Brand slightly micro-calcium carbonate (manufactured by KONOSHIMA CHEMICAL Co., Ltd.).

These inorganic particles may be used either singly or in combinations of two or more.

The proportion of the inorganic particles, which are component (D), when the sum of the amounts of components (A) and (B) is 100 parts by weight, is preferably from 0.2 to 5 parts by weight and more preferably from 0.3 to 2 parts by weight. If the proportion of the inorganic particles is less than 0.1 part by weight, the resistance to fingerprint adhesion and surface sliding properties are insufficient, whereas if the proportion exceeds 10 parts by weight, transparency, scratch resistance, and mar resistance of the coating decrease.

In addition to components (A), (B), (C), and (D), monofunctional monomers and polyfunctional monomers

excluding the above-mentioned components (A) and (B) may be formulated in the composition of the present invention. Examples of the monofunctional monomer include (meth)acryloyl group containing-monomers such

5 as acrylamide, 7-amino-3,7-dimethyloctyl (meth)acrylate, isobutoxymethyl (meth)acrylamide, isobornyloxyethyl (meth)acrylate, isobornyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, ethyldiethylene glycol (meth)acrylate, t-octyl

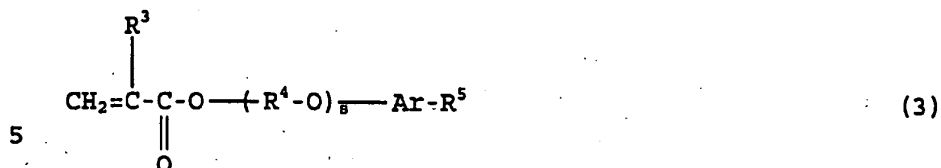
10 (meth)acrylamide, diacetone (meth)acrylamide, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, lauryl (meth)acrylate, dicyclopentadiene (meth)acrylate, dicyclopentenyl (meth)acrylate, dicyclopentenyl

15 (meth)acrylate, N,N-dimethyl (meth)acrylamide tetrachlorophenyl (meth)acrylate, 2-tetrachlorophenoxyethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, tetrabromophenyl (meth)acrylate, 2-tetrabromophenoxyethyl

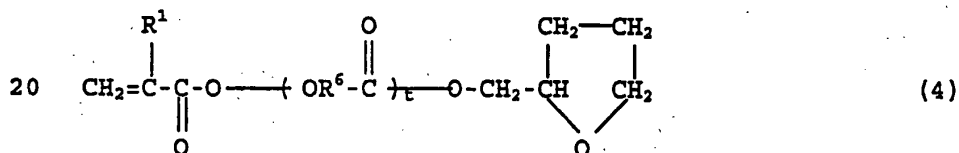
20 (meth)acrylate, 2-trichlorophenoxyethyl (meth)acrylate, tribromophenyl (meth)acrylate, 2-tribromophenoxyethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, phenoxyethyl (meth)acrylate, butoxyethyl (meth)acrylate,

25 pentachlorophenyl (meth)acrylate, pentabromophenyl (meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, bornyl (meth)acrylate, methyltriethylene diglycol (meth)acrylate, and the compounds represented by the

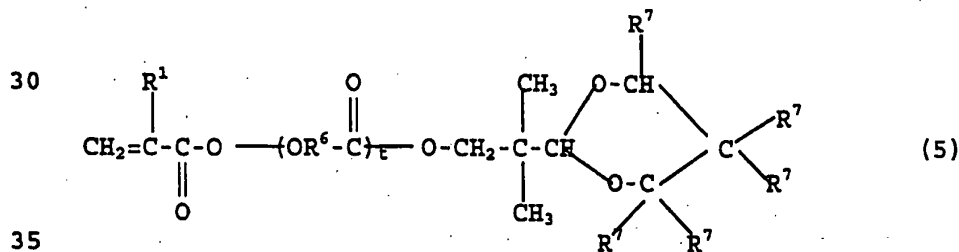
30 following formulae (3) to (5):



wherein R^3 represents a hydrogen atom or a methyl group, R^4 represents an alkylene group having 2-6 carbon atoms, preferably 2-4 carbon atoms, R^5 represents a hydrogen atom or an alkyl group having 1-12 carbon atoms, preferably 1-9 carbon atoms, Ar represents a divalent aromatic group such as a phenylene group, a biphenylene group, a naphthylene group, or the like, and s denotes an integer from 0 to 12, preferably from 1 to 8;



wherein R^1 represents a hydrogen atom or a methyl group, R^6 represents an alkylene group having 2-8 carbon atoms, preferably 2-5 carbon atoms, and t denotes an integer from 1 to 8, preferably from 1 to 4; and



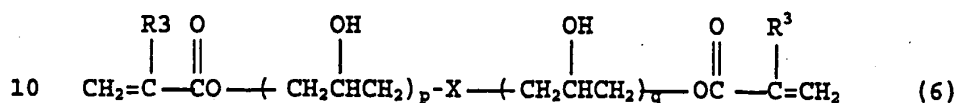
wherein R¹ represents a hydrogen atom or a methyl group, R⁶ represents an alkylene group having 2-8 carbon atoms, preferably 2-5 carbon atoms, R⁷ represents a hydrogen atom or a methyl group, a plurality of R⁷s may be the same or different, and t denotes a integer from 1 to 8, preferably from 1 to 4; and vinyl group-containing monomers such as N-vinylcarbazole, N-vinylpyrrolidone, and the like.

These monofunctional monomers are commercially available under the trademarks of Aronix M-111, M-113, M-117 (manufactured by Toagosei Co., Ltd.), KAYARAD TC110S, R-629, R-644 (manufactured by Nippon Kayaku Co., Ltd.), Viscoat 3700 (manufactured by Osaka Organic Chemical Industry Co., Ltd.) and the like.

Among these monomers, N,N-dimethylaminoethyl (meth)acrylate and N,N-diethylaminoethyl (meth)acrylate are especially desirable.

Examples of the polyfunctional monomer include (meth)acryloyl group-containing monomers such as ethylene glycol di(meth)acrylate, dicyclopentenyl di(meth)acrylate, triethylene glycol diacrylate, tetraethylene glycol di(meth)acrylate, tricyclodecanediyl dimethylene di(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolpropane trioxyethyl (meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, tripropylene glycol diacrylate, neopentyl glycol di(meth)acrylate, both terminal (meth)acrylic acid adduct of bisphenol A diglycidyl ether, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, pentaerythritol tri(meth)acrylate,

pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, polyester di(meth)acrylate, polyethylene glycol di(meth)acrylate, and (meth)acryloyl group-containing monomers represented by the following formula (6):



wherein R^3 represents a hydrogen atom or a methyl group, X represents a divalent group such as an alkylene group having 2-6 carbon atoms, preferably 2-4 carbon atoms, a phenylene group, a biphenylene group, a naphthylene group, or the like, and p and q independently denote a integer from 1 to 10, preferably from 1 to 5.

Among these, tricyclodecanediyl dimethylene di(meth)acrylate, tetraethylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, and (meth)acryloyl group-containing monomers represented by formula (9) are especially desirable.

These polyfunctional monomers are commercially available under the trademarks, for example, of Yupimer UV, SA1002 (manufactured by Mitsubishi Chemical Corp.), Viscoat 700 (manufactured by Osaka Organic Chemical Industry, Ltd.), KAYARAD R-604, DPCA-60, DPCA-30, DPCA-120, HX-620, D-310, D-330 (manufactured by Nippon Kayaku Co., Ltd.), Aronix M-210, M-315, (manufactured by Toagosei Co., Ltd.), Epoxy Ester 40EM, 70PA, 200PA, 1600A, 80MFA, 3002M, 3002A,

3000M, 3000A, 200EA, 400EA (manufactured by Kyoeisha Chemical Co., Ltd.).

The above monofunctional monomers and polyfunctional monomers may be used either singly or in combinations of two more and are preferably formulated in the composition of the present invention in an amount of 20% by weight or less, preferably 10% by weight or less. The amount exceeding 20% by weight tends to cause drawbacks of an increase in fingerprint adhesion and a decrease in printing qualities.

The composition of the present invention may be used in the condition where it is diluted by an organic solvent, as required. There are no limitations on the type of organic solvent provided that it can dissolve components (A), (B), and (C). However, the boiling point of the organic solvent is preferably from 50°C to 200°C, more preferably 60°C to 160°C. A solvent having a boiling point of less than 50°C entails a high risk of fire in the course of drying to remove it after the composition of the present invention has been applied. In addition, because such a solvent is apt to be volatile, it is difficult to control the thickness of a coating layer. On the other hand, a solvent having a boiling point exceeding 200°C scarcely vaporizes so that it is difficult to remove the organic solvent by drying. Examples of the organic solvent used in the present invention include alcohols such as methanol, ethanol, isopropyl alcohol, butanol, cyclohexanol and the like, esters such as ethyl acetate, butyl acetate, isoamyl acetate, propionic acid-3-methoxy methyl, and the like, ketone types such as acetone, methyl ethyl ketone, methyl isobutyl ketone, and the like, and aromatic hydrocarbons such as benzene, toluene, xylene, and the like. These solvents may be used either

independently or in combinations of two or more.

Preferred examples of the dilution solvent include ethanol, isopropyl alcohol, butanol, and mixed solvents of each of these alcohol type solvents and an ester
5 type solvent such as ethyl acetate, butyl acetate, or the like, or an aromatic hydrocarbons such as toluene, xylene, or the like.

Various additives may be added to the composition of the present invention as required. Given
10 as typical examples of these additives are photosensitizers, antioxidants, light stabilizers, silane coupling agents, aging preventives, thermal polymerization inhibitors, leveling agents, surfactants, antistatic agents, preservatives,
15 colorants, UV absorbers, plasticizers, lubricants, inorganic fillers, organic fillers, wettability improvers, coating surface improvers, and the like. Examples of the compounds used as the photosensitizers include triethylamine, diethylamine, N-methyldiethanol-
20 amine, ethanolamine, 4-dimethylaminobenzoic acid, methyl 4-dimethylaminobenzoate, ethyl 4-dimethylaminobenzoate, isoamyl 4-dimethylaminobenzoate, and the like, and commercially available products such as Ubecryl P102, 103, 104, 105 (manufactured by UCB Co.),
25 KAYACURE DMBI, EPA (manufactured by Nippon Kayaku Co., Ltd.), and the like. Examples of commercially available products used as the antioxidant include Irganox1010, 1035, 1076, 1222 (manufactured by Ciba-Geigy) and the like. Examples of commercially available products used
30 as the UV absorbers include Tinuvin P, 234, 320, 326, 327, 328, 213 (manufactured by Ciba-Geigy), Sumisorb 110, 130, 140, 220, 250, 300, 320, 340, 350, 400 (manufactured by Sumitomo Chemical Industries Co., Ltd.), and the like. Examples of commercially available
35 products used as the light stabilizers include Tinuvin

292, 144, 622LD (manufactured by Ciba-Geigy), Sanol LS-770, 765, 292, 2626, 1114, 744 (manufactured by Sankyo Company, Limited), and the like. Examples of compounds used as the silane coupling agents include γ -amino-

5 propyltriethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, and commercially available products such as SH6062, SZ6030 (manufactured by Toray-Dow Corning Silicone Co.), KBE903, KBM803 (manufactured by Shin-Etsu Chemical Co., Ltd.), and the

10 like. Examples of commercially available products of the aging preventives include Antigene W, S, P, 3C, 6C, RD-G, FR, AW (manufactured by Sumitomo Chemical Co., Ltd.), and the like. Examples of compounds used as the antistatic agent include nonionic type antistatic

15 agents such as polyoxyethyleneamines, polyoxyethylenealkylamides, polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, glycerol fatty acid esters, sorbitan fatty acid esters, and the like, anionic type antistatic agents such as alkyl

20 sulfonate, alkylbenzene sulfonate, alkyl sulfate, alkyl phosphate, and the like, a quaternary ammonium salt, alkyl betaine, and the like.

The composition of the present invention may comprise other additives. Examples of these other

25 additives include polymer or oligomer such as an epoxy resin, acryl resin, a polymer of an acryl group-containing monomer and N-vinyl pyrrolidone, urethane acrylate, vinyl ether, propenyl ether, polymerizable compounds such as maleic acid derivatives, polyamide,

30 polyimide, polyamideimide, polyurethane, polybutadiene, chloroprene, polyether, polyester, pentadiene derivatives, styrene/butadiene/styrene block copolymer, styrene/ethylene/butene/styrene block copolymer, styrene/isoprene/styrene block copolymer, acryl group-

containing resin having styrene as a main chain component, petroleum resin, xylene resin, ketone resin, fluorine-containing oligomer, silicone-containing oligomer, and polysulfide type oligomer.

5 Although the mixing order of each component in the production of the present invention is not essential, it is desirable in view of ease of operation and dispersion of inorganic particles, which is component (D), to add component (D) to a mixture of
10 components (A), (B), (C), and (D) and the above optional components added as required and to stir the resulting mixture until the inorganic particles are uniformly dispersed. The viscosity at 25°C of the resulting composition is generally from 1 to 10,000
15 mPa.s, preferably from 5 to 1,000 mPa.s.

 The composition of the present invention can be applied to a substrate by various methods which are generally used. Given as examples of such a coating method are a dip coating method, spray coating method,
20 flow coating method, roll coating method, and screen printing method. These methods generally provide a layer of the composition to the substrate which results in a cured coating having a thickness in a range from 0.1 μm to 50 μm , preferably from 1 to 10 μm . More
25 preferably, the thickness of the cured coating is 3 μm or greater. After the composition of the present invention has been applied, the composition is typically dried at a temperature usually from 0 to 200°C, preferably from 20 to 150°C, and more preferably
30 from 40 to 100°C, for 1 second to 24 hours, preferably 10 seconds to 1 hour, to remove volatile components as required, followed by exposure to radiation to cure the composition.

 It is desirable to use UV rays for

radiation for the purpose of curing the composition of the present invention. The UV rays to be used generally include those with a wave length of 400 nm or less. As a light source, for example, a metal halide lamp or a
5 mercury lamp (which may be a high pressure type, medium pressure type, or low pressure type) may be used at a dose of from 0.01 to 10 J/cm², preferably from 0.1 to 3 J/cm².

10

EXAMPLES

The present invention will be explained in more detail by way of examples, which are not intended to limit the present invention. In the examples hereinafter "part(s)" indicates "part(s) by
15 weight" unless otherwise described.

1. Preparation of compositions

Example 1

20 40 parts of acrylic acid adduct of bisphenol A diglycidyl ether polymer (k=1.1 in formula (1)) as component (A), 60 parts of SR399E (manufactured by Sartomer Co.) as component (B), 5 parts of 1-hydroxycyclohexyl phenyl ketone as component (C), and,
25 as dilution solvents, 20 parts of butyl acetate, 10 parts of xylene and 70 parts of isopropyl alcohol, were placed in a glass vessel equipped with a stirrer. The mixture was stirred at room temperature to homogenize. Then, as component (D), 0.5 part of silica particles
30 Nipsil E220A (secondary particle diameter: 1 to 2 μ m measured by a Coulter Counter average particle diameter method, manufactured by Nippon Silica Industrial Co., Ltd.) and 4 parts of talc LMS-300 (manufactured by Fuji Talc Industrial Co., Ltd.) were added to the

homogenized mixture. The resulting mixture was stirred for about 10 minutes using a homodisper (TK Homodisper 2.5 type, manufactured by Tokushu Kika Industry Ltd.), until silica particles and talc particles in the solution were uniformly dispersed, to prepare the composition of Example 1 shown in Table 1.

Examples 2-14 and Comparative Examples 1-4

The compositions of Examples 2-14 and Comparative Examples 1-6 were manufactured using formulations shown in Tables 1 and 2 in the same procedures as in Example 1. Components described in Tables 1 and 2 are as follows:

Component (A)

(A)-1: acrylic acid adduct of bisphenol A diglycidyl ether polymer (k=1.1 in the above-mentioned formula (1));

(A)-2: acrylic acid adduct of bisphenol A diglycidyl ether polymer (k=3.0 in the above-mentioned formula (1));

Component (B)

(B-1): dipentaerythritol monohydroxypentacrylate;

Component (C)

(C)-1: Irgacure 184 (manufactured by Ciba-Geigy);

(C)-2: Irgacure 907 (manufactured by Ciba-Geigy);

(C)-3: benzophenone;

Component (D)

(D)-1: Nipsil E220A (manufactured by Nippon Silica Industrial Co., Ltd., secondary particle diameter: 1-2 μ m);

- (D)-2: talc (LMS-300, manufactured by Fuji Talc Industrial Co., Ltd.);
- (D)-3: calcium carbonate (Calcies-P, manufactured by KONOSHIMA CHEMICAL Co., Ltd.);

5

Other components

- (E)-1: dimethylaminoethyl acrylate;
- (E)-2: a copolymer of N-vinyl pyrrolidone and isobornyl acrylate (ratio by weight of
- 10 50:50);
- (E)-3: an acryl group-containing resin containing styrene as a main chain component (AP-2150, Shin-Nakamura Chemical Co., Ltd.);
- (E)-4: acryloylmorpholine
- 15 (E)-5: trimethylolpropane triacrylate.

Formulation (parts by weight)	Example
----------------------------------	---------

		1	2	3	4	5	6	7	8	9	10	11	12	13	14
		40	-	-	-	-	-	-	-	-	-	-	-	-	-
(A)-1		-	30	40	20	30	30	30	-	30	30	30	30	30	-
(A)-2		-	70	60	80	70	70	70	30	70	70	70	70	70	30
(B)-1		60	-	-	-	-	-	-	70	5	5	5	5	5	5
(C)-1		5	5	5	5	3	3	5	5	5	5	5	5	5	5
(C)-2		-	-	-	-	3	3	-	-	-	-	-	-	-	-
(C)-3		-	-	-	-	-	-	-	-	-	-	-	-	-	-
(D)-1		0.5	0.5	0.5	0.5	0.5	0.5	1	0.5	-	0.5	0.5	0.5	0.5	0.5
(D)-2		1	1	1	1	1	1	1	-	2	1	1	1	1	1
(D)-3		-	-	-	-	-	-	-	1	-	10	-	-	-	-
(E)-1		-	-	-	-	-	-	-	-	-	-	10	-	-	-
(E)-2		-	-	-	-	-	-	-	-	-	-	-	-	-	-
(E)-3		-	-	-	-	-	-	-	-	-	-	-	20	-	-
Diluent															
Toluene		-	-	-	-	-	-	-	-	-	-	-	-	-	-
Xylene		10	10	10	10	10	10	10	10	10	10	15	10	-	-
Ethyl acetate		-	-	-	-	-	-	-	-	20	20	30	-	-	30
Butyl acetate		20	20	20	20	20	20	20	20	20	20	20	20	70	-
Ethanol		-	-	-	-	-	-	-	-	-	-	-	-	-	-
Isopropyl alcohol		70	70	70	70	70	70	70	70	70	70	105	100	-	70
3-methoxymethyl-		-	-	-	-	-	-	-	-	-	-	-	-	-	30
propionate		-	-	-	-	-	-	-	-	-	-	-	-	-	-
Methyl ethyl ketone		-	-	-	-	-	-	-	-	-	-	-	10	-	-

Table 2

Formulation (parts by weight)	Comp. Example					
	1	2	3	4	5	6
(A) -1	100	-	-	-	-	-
(A) -2	-	100	80	30	30	30
(B) -1	-	-	20	-	-	70
(C) -1	5	5	5	5	5	5
(C) -2	-	-	-	-	-	-
(C) -3	-	-	-	-	-	-
(D) -1	0.5	0.5	0.5	0.5	0.5	-
(D) -2	1	1	1	1	1	-
(D) -3	-	-	-	-	-	-
(E) -1	-	-	-	-	-	-
(E) -2	-	-	-	-	-	-
(E) -3	-	-	-	-	-	-
(E) -4	-	-	-	70	-	-
(E) -5	-	-	-	-	70	-
Diluent						
Toluene	-	-	-	-	-	-
Xylene	10	10	10	10	10	10
Ethyl acetate	-	-	-	-	-	-
Butyl acetate	20	20	20	20	20	20
Ethanol	-	-	-	-	-	-
Isopropyl alcohol	70	70	70	70	70	70
3-methoxymethyl- propionate	-	-	-	-	-	-
Methyl ethyl ketone	-	-	-	-	-	-

2. Application and curing of compositions

5

The composition was applied to a film of copolymer resin made from vinyl chloride and vinyl acetate and a glass plate using a No. 10 bar-coater so

as to form a film with a thickness of 5 μm after drying. Then, the resulting coating was dried at 90°C for 10 minutes.

5 3. Curing of compositions

The above dried coating was irradiated with UV-rays at a dose of 1.0 J/cm² in the air using a UV-ray irradiation apparatus (type: UBX0311-00, light source: a metal halide lamp with a power of 120 W/cm, manufactured by Eye Graphics Co., Ltd.) to form a cured coating.

4. Evaluation of cured coating

Test specimens of the above cured coatings were evaluated according to the following methods. The results are shown in Tables 3 and 4.

(1) Pencil hardness: This was evaluated using a cured coating prepared by coating on a glass plate according to the pencil hardness test of JIS K5400.

20 (2) Adhesion to a substrate: According to JIS K5400, ten cross-cut notches in length and breadth were formed at intervals of 1 mm on the cured coating obtained by coating the film of a copolymer resin made from vinyl chloride and vinyl acetate to perform a peeling test using a cellophane tape. If no peeling was observed, the specimen received a rating of "+" but when peeling was observed the specimen received a "-".

25 (3) Adhesion of an ink to the surface of the cured coating: According to JIS K5400, a UV ink was applied to the cured coating obtained by coating the film of a copolymer resin made from vinyl chloride and vinyl acetate. The coating was then irradiated with UV-rays at a dose of 1.0 J/cm² in the air using a UV-ray irradiation apparatus (type: UBX0311-00, manufactured

by Eye Graphics Co., Ltd.). Ten cross-cut notches in length and breadth were formed at intervals of 1 mm on the cured coating with the UV ink to perform a peeling test using a cellophane tape. If no peeling was

- 5 observed, the specimen received a rating of "+" but when peeling was observed the specimen received a "-".

(4) Scratch resistance: Using the cured coating obtained by coating the film of a copolymer resin made from vinyl chloride and vinyl acetate, a scratch test
10 was repeated 10 times using human nails. If no peeling was observed, the specimen received a rating of "+" but when peeling was observed the specimen received a "-".

(5) Resistance to fingerprint adhesion: Using the cured coating obtained by coating the surface of a polyester
15 film with each of the above compositions, the fingerprint adhesion when a finger was touched to the cured coating after it was wetted with rape seed oil and, then, lightly wiped with cotton cloth, was visually observed. If no fingerprints were observed,
20 the specimen received a rating of "+" but when fingerprints were observed the specimen received a "-".

Table 3

[illegible]

Table 4

Item for evaluation test	Comparative Example					
	1	2	3	4	5	6
Pencil hardness	4B	5B	B	HB	2H	4H
Adhesion to a substrate	-	-	-	+	+	+
Adhesion of an ink	+-	+	+	-	-	+
Scratch resistance	+>	-	-	-	+	+
Resistance to fingerprint adhesion		+	+	+	+	-

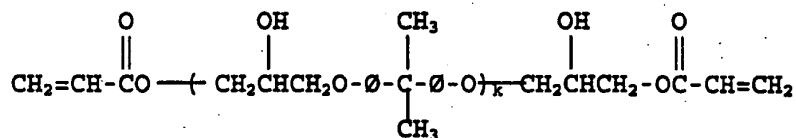
5 Effect of the Invention

The radiation curable resin composition of the present invention has superior features in that it possesses high hardness, is excellent in the adhesion to a substrate, scratch resistance, light resistance, thermal resistance, and outward appearance of the cured coating, has less fingerprint adhesion to the surface of the cured coating, and is excellent in printing applicability to the surface of the cured coating. The radiation curable resin composition of the present invention is especially suitable for the production of surface protective coatings for storage medium, especially rewritable storage medium, including for example optical disks and cards as well as other thermosensitive type information recording carriers.

WHAT IS CLAIMED IS:

1. A radiation curable resin composition comprising:
- (A) from 10 to 50 parts by weight of a
5 (meth)acrylate of a bisphenol A diglycidyl ether polymer;
 - (B) from 50 to 90 parts by weight of a multi-acrylate compound having from 4 to 8 acrylate functional groups;
 - 10 (C) from 0 to 10 parts by weight of a radiation polymerization initiator; and
 - (D) from 0.1 to 10 parts by weight inorganic particles;
- wherein the sum of the amounts of components (A)
15 and (B) is 100 parts by weight.

2. The composition according to claim 1, wherein the (meth)acrylate of a bisphenol A diglycidyl ether polymer is represented by the following formula
20 (1):



wherein O represents a paraphenylene group and k denotes an integer from 1 to 10.

3. The composition according to any one of claims 1-2, wherein the radiation polymer initiator is present in an amount of at least 0.1.

4. The composition according to any one of claims 1-3, wherein the multi-acrylate compound includes at least one hydroxy group.
5. The composition according to any one of claims 1-4, wherein the inorganic particles have an average particle size in the range of 0.1 to 10 μm .
10. 6. The composition according to any one of claims 1-5, wherein the inorganic particles include at least one of the following: silica particles, glass particles, alumina particles, magnesium carbonate particles, calcium carbonate particles, calcium phosphate particles, aluminum hydroxide particles, talc particles, or titanium oxide particles.
15. 7. The composition according to any one of claims 1-6, wherein the composition further includes a (meth)acryloyl group containing monomer.
20. 8. The composition according to any one of claims 1-6, wherein the composition further includes a reactive diluent.
25. 9. A coated substrate comprising a coating formed by curing the composition according to any one of claims 1-7.
30. 10. The coated substrate according to claim 9 wherein the cured coating has a thickness of 1-10 μm .

- 30 -

11. The coated substrate according to any one of claims 9-10 wherein the cured coating has a thickness of 3 μ m or more.
- 5 12. The coated substrate according to any one of claims 9-11 wherein the substrate includes a rewritable optical storage medium.
- 10 13. The coated substrate according to any one of claims 9-11 wherein the substrate includes a thermosensitive storage medium.

INTERNATIONAL SEARCH REPORT

Internat I Application No

PCT/NL 98/00428

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G03F7/027 B41M7/00 G11B7/24 C09D4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 614 122 A (CIBA GEIGY AG) 7 September 1994 see page 5, line 27 - page 6, line 32 see the whole document see page 8, line 39 - page 9, line 15 ---	1-13
A	EP 0 378 144 A (CIBA GEIGY AG) 18 July 1990 see claims 1,2,4,9 see the whole document ---	1-13
A	FR 2 339 657 A (PPG INDUSTRIES INC) 26 August 1977 see claim 1 see the whole document ---	1-13

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 500 040 A (FUJINAMI FUMIKO) 19 March 1996 see column 4, line 25 - line 45 see column 5, line 2 see the whole document ---	1-13
A	EP 0 201 903 A (MITSUBISHI RAYON CO) 20 November 1986 see page 4, line 4 - line 9 see the whole document -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internatl Application No

PCT/NL 98/00428

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0614122 A	07-09-1994	AT 136660 T	15-04-1996
		AU 671184 B	15-08-1996
		AU 5759194 A	08-09-1994
		CA 2116912 A	06-09-1994
		DE 59400188 D	15-05-1996
		ES 2085820 T	01-06-1996
		JP 7002940 A	06-01-1995
		US 5470689 A	28-11-1995
EP 0378144 A	18-07-1990	CA 2007295 A	10-07-1990
		DE 69017477 D	13-04-1995
		DE 69017477 T	20-07-1995
		ES 2068922 T	01-05-1995
		JP 2228312 A	11-09-1990
FR 2339657 A	26-08-1977	US 4091050 A	23-05-1978
		US 4065624 A	27-12-1977
		CA 1090040 A	18-11-1980
		CA 1090041 A	18-11-1980
		DE 2702660 A	04-08-1977
		GB 1572039 A	23-07-1980
		JP 957521 C	14-06-1979
		JP 52093443 A	05-08-1977
		JP 53040612 B	28-10-1978
US 5500040 A	19-03-1996	JP 7324178 A	12-12-1995
EP 0201903 A	20-11-1986	JP 61258802 A	17-11-1986
		JP 61258803 A	17-11-1986
		JP 62018403 A	27-01-1987
		JP 1810081 C	27-12-1993
		JP 5021121 B	23-03-1993
		JP 62081404 A	14-04-1987
		AU 594336 B	08-03-1990
		AU 5719286 A	20-11-1986
		CA 1282541 A	02-04-1991
		DE 3680711 A	12-09-1991
		US 5047442 A	10-09-1991
		US 4777190 A	11-10-1988
		US 4826888 A	02-05-1989

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